Patent Application of

Michael McBrearty and Anthony J. Bur

For

TITLE: A DIELECTRIC SLIT DIE FOR IN-LINE MONITORING OF LIQUIDS PROCESSING

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims benefit of Provisional Patent Application Serial No. 60/461668 filed April 11, 2003. This application uses the frammis vane disclosed in patent 5,208,544 granted May 4, 1993 and patent 5,519,211 granted May 21, 1996 and patent 5,788,374 granted Aug. 4, 1998.

FEDERALLY SPONSORED RESEASRCH

This invention was developed under sponsorship of the National Institute of Standards and Technology, Gaithersburg, MD

REFERENCE TO SEQUENCE LISTING, A TABLE, OR COMPUTER PROGRAM

Not Applicable

BACKGROUND OF INVENTION – FIELD OF INVENTION

This invention relates to multiple sensor monitoring of materials properties of liquids during processing – particularly to the dielectric, optical and ultrasonics properties of molten polymer composites that are processed using an extruder machine.

BACKGROUND OF INVENTION

Many products are formulated by mixing liquid components together and by mixing liquids and solids together. Efficient manufacturing methods usually involve continuous processing whereby components are fed into a process line at one end, are mixed and then are transported by means of pipes and conveyor belts to post processing handling and examination. The properties of the final product are determined by recipes of component content, mixing time, temperature, pressure, chemistry and other process parameters. Often these recipes are complex and need to be monitored continuously in order to maintain product quality. The current practice for many processes is to examine product quality after the product has been made. In many cases, post-processing examination takes days or weeks to complete. On-line, real-time processing will eliminate the knowledge delay about the process, allow for immediate correction of process problems and be a sentry for the maintaining process integrity and product quality.

On-line process sensors of many types have been developed. These include ultrasonics, optics, rheological, and dielectric sensors. Applications of these sensors have involved installations of a single sensor with a focus on one material property. Multifunctional sensing with several sensors installed in an on-line chamber with multiple sensor ports is not currently practiced. For processing of complex liquids such as polymer composites, foodstuffs, and mixtures in slurries, multiple sensing is needed because a single sensor such as temperature or pressure does not provide enough information to assess the condition and quality of the product. Each sensor has its assets and limitations whereas

multiple sensors provide a collection of data, which, when integrated together, potentially yield a critical level of information.

This invention not only addresses the need for more information about the processes and the material being processed, it also presents an improvement of the dielectric sensor design of McBrearty and Perusich. The dielectric sensor of this invention is of the interdigitating electrode type, a concept that was developed by Senturia and subsequently commercialized by Micromet. Kranbuehl refined the measuring technique and the sensor so that the real and imaginary parts of the dielectric constant ε' and ε'' could be measured using a network analyzer. The Senturia and Kranbuehl sensors were used primarily at low temperatures and in benign environments and are not suitable for measuring abrasive, molten plastics processed under flow at high temperatures and pressures. High temperature dielectric monitoring of highly viscous molten plastic was accomplished by McBrearty and Perusich who used a ceramic ring with interdigitating electrodes deposited and fired onto the inside of the ring. Dielectric properties of fluids flowing through the ring are measured. The design of the McBrearty and Perusich cell consists of the ceramic ring sandwiched between high temperature gaskets that are bolted between two stainless steel cylinders, and the entire housing is wrapped with temperature controlled heater bands. When connected to a process extruder or pump, the gaskets provide a leak-proof, flow-through cell for processing liquids under pressure.

The problem with the ceramic ring design is the limited extent to which the fringe field can interrogate the flowing liquid. For example, a ring with 12.7 mm inside diameter and having electrode separation $\lambda = 0.5$ mm can interrogate only a thin shell near the electrodes that amounts to 15 % of the cross section of the liquid flow stream. This is because the electric fringing field from the interdigitating electrodes decreases exponentially in intensity from the electrode surface with a characteristic length of $\lambda/3$. If λ is made larger in order to extend the fringe field, the sensitivity of the cell is diminished because of decreased capacitance. Sampling only 15 % of the processed liquid is not satisfactory because it may not be representative of the total bulk properties.

Other problems with the ceramic ring design are the gaskets that are placed on either side of the ceramic ring in order to seal the unit and protect it from leaks. When processing polymers, these gaskets must perform at high temperatures for long periods of time. They are made of a specialty compound and they are expensive to replace as is needed during the normal course of operation.

It is the purpose of this invention to provide a common platform in a process line on which multiple sensors can be installed. Also, an integral part of this invention is an improved dielectric sensor. The dielectric sensor of this invention retains the robustness of the ceramic substrate used by McBrearty and Perusich while adding flexibility and new capabilities. The electroded ceramic substrate is used in an innovative slit design that incorporates complementary sensors and slit geometry while eliminating gaskets. Also, the design permits interchangeable ceramic substrates with different electrode patterns and electrode separation λ. The common platform is a slit through which processed liquids flow. The slit is made long enough to accommodate the sensors that access the liquid flowing therein. The slit defines a sample chamber of constant volume that is continuously being replenished by new material as the liquid flows into and out of the slit.

The advantages of this invention are: (a) the slit configuration that confines the flowing liquid to a thin ribbon for which a significant fraction of its cross section is intersected by the fringing electric field lines; (b) the slit configuration that defines a sample chamber of fixed dimensions along which other sensors can be positioned; (c) the slit is the geometry of a slit die rheometer so that with knowledge of the pressure drop across the length of the slit and the volume flow rate, the viscosity of the material can be determined; (d) the simplicity of design eliminates gaskets and adhesives in the assembly; (e) the interchangeability of parts permits the use of different electrode patterns to measure near surface, bulk and orientation effects in the dielectric phenomena; (f) the flexibility of design permits the addition of new sensors and sensor port sectors in line with the dielectric slit die; and (g) because the slit shape confines fluid flow by applying shear

stress to the fluid, this design decreases the transition time for flushing the slit volume of the old liquid when making a change in the process from one composition to another.

This invention fulfills a need in liquids processing that will produce improved product quality and productivity. Commercial applications of this device cut across many industries in which liquids are mixed and processed according to a formula that must be continually monitored in order to maintain product quality. Plastics, paints, cosmetics, chemicals, pharmaceuticals, building products, food and beverage industries can utilize this invention because it can be used to determine mixture ratios and important materials properties such as electrical, optical, and rheological properties. Knowledge of these materials properties can be used to predict product performance and to understand and control the process.

BREIF SUMMARY

The dielectric slit die is a multifunctional instrument that is used to measure the materials properties of liquid materials while they are being processed in a continuous flow stream. In one application, it is connected to the exit of an extruder, pump or mixing machine that passes liquefied material such as molten plastic, solvents, slurries, colloidal suspensions, and foodstuffs into the sensing region of the slit shaped die. The dielectric slit die has a steel housing that contains instrument ports for a plurality of sensors to access the flowing liquid. In this design the slit forms a platform of uniform dimensions upon which multiple sensors can be mounted. Dielectric sensing is the primary sensor of the slit die, but in addition, the die contains other sensing devices such as pressure, optical fiber, and ultrasonic sensors that simultaneously yield an array of materials property data. The slit die has a flexible design that permits interchangeability among sensors and sensor positions and permits changes in the slit dimensions. The design also allows for the placement of additional sensors and instrumentation ports that expand the potential data package obtained. A plurality of sensors comprising a dielectric sensor, a temperature sensor, a pressure sensor, an optical sensor, an ultrasonics sensor and any

sensor that can be used to measure the material properties of the flowing liquid are candidate measuring tools.

The dielectric sensor is an interdigitating electrode type where the interdigitated electrodes are deposited on a flat ceramic substrate that forms one surface of the slit. When a voltage is applied to the electrodes, a fringing electric field reaches into the liquid flow stream as it traverses the slit. By measuring the in-phase and out-of-phase current flowing in the liquid, it is possible to calculate the dielectric permittivity and the dielectric loss of the processed liquid. The optical sensor consists of a sensor bolt that can be inserted into the standard half-inch instrument port that exists on many processing machines. The sensor bolt is a sleeve with a sapphire window at its end that can receive an optical fiber for transmitting light through the sapphire window. When inserted into the instrument port, the sapphire window sits flush with the surface of the slit and optical sensing of the flowing liquid is achieved. Light reflected back from the opposite wall of the slit and into collection optical fibers is used to measure optical transmission. When a fluorescent dye is mixed with the flowing liquid, a spectrum can be obtained by connecting the collection optical fibers to a monochromator. A pressure sensor at an upstream position in the slit will yield the pressure drop in the slit from which the viscosity of the liquid can be obtained when the flow rate is known. The objective of using multiple sensors is to obtain simultaneous information about the processed liquid so that the process can be controlled and material specifications can be maintained. The dielectric slit die is designed as a robust manufacturing unit that can be used for processing abrasive polymer composites at high process temperatures and pressures.

DRAWINGS

Figure 1a is a side view of the dielectric slit die showing the sensor ports and the ceramic substrates of the dielectric sensor.

Figure 1b is a front view of the dielectric slit die.

Figure 2 shows the dielectric slit die attached to an extrusion machine.

Figure 3 shows the basic interdigitating electrode arrangement that is deposited on a ceramic substrate.

Figure 4a shows two interdigitating electrode patterns deposited on the same ceramic substrate. The two patterns have different electrode separations that create fringing fields closer and farther from the surface of the ceramic.

Figure 4b shows two interdigitating electrode patterns that are oriented at 90° with respect to each other creating fringing electric fields that are oriented at 90° with respect to each other.

Figure 5 is a drawing of an optical sensor bolt that has been machined to receive an optical fiber, a focusing lens and a sapphire window at its end.

Figure 6 is a diagram of the optics setup used for measuring light transmission and fluorescence. PMT refers to photomultiplier tube.

Figure 7 shows the position of the additional sensor sector that can be added to the sensor train in order to employ more sensors.

Figure 8a shows the relative permittivity for the nylon 12, nylon 12 compounded with clay filler, and polyethylene versus time at 15 frequencies between 500 Hz and 10^5 Hz. The materials were extruded at 195 °C.

Figure 8b shows dielectric loss for the nylon 12, nylon 12 compounded with clay filler, and polyethylene versus time at 15 frequencies between 500 Hz and 10^5 Hz. The materials were extruded at 195 °C.

Figure 9a shows the pressure drop along the slit versus time for extrusion of nylon 12, nylon 12 compounded with clay filler, and polyethylene. The data are from the same experiment as Figures 8a and 8b and 9b.

Figure 9b shows light transmission versus time for extrusion of nylon 12, nylon 12 compounded with clay filler, and polyethylene. The data are from the same experiment as Figures 8a and 8b and 9a.

Figure 10 is a plot of intensity versus wavelength for a fluorescent dye benzoxazolyl stilbene that was compounded with polyethylene-vinyl acetate copolymer. The dye was excited with 365 nm wavelength light. The material was extruded at 150 °C

DETAILED DESCRIPTION OF PATENT

The dielectric slit die **1** is a real-time process monitoring device for measuring material properties of flowing liquids. It is designed to attach to the exit of an extruder or pump that forces a processed liquid through a slit channel under pressure. The slit channel **2**, with dimensions of 2 mm high by 2.8 cm wide by approximately 17 cm in length, defines a constant geometry sample cell in which the processed material is examined by on-line sensing devices. The primary sensor in the channel is the dielectric sensor consisting of interdigitated electrodes **3** that are deposited onto a ceramic substrate **4**. The current configuration of this invention includes pressure, optical fiber, and ultrasonic sensors, but its flexible design allows for the addition of new sensors and instrumentation ports, and permits the interchange of sensors to different positions in the slit channel.

A schematic diagram of the dielectric slit die is shown in Figures 1a and 1b. All sensors in the slit die are contained in a cylindrical stainless steel housing that consists of upper **5** and lower **6** halves. It contains threaded instrumentation ports **7** and **30** of the standard half-inch by 20 threads-per-inch type in addition to two cut out chambers **8** and **9** for ceramic in-lays that are used for dielectric sensing. The ceramic piece on the bottom **4** is high purity alumina onto which platinum electrodes have been deposited and fired in an interdigitating pattern **3**. The ceramic **10** in the top half is made from a machinable ceramic, has a trapezoidal cross section, and contains a cutout of the slit channel **2** that is 2mm deep by 2.8 cm wide extending over the length of the piece that is approximately 11 cm. The trapezoidal cross section serves to hold the piece into place in the top half stainless steel piece **5**. The entire slit die unit, which is 12.7 cm in diameter by approximately 17 cm long, is wrapped with temperature controlled heater bands **11**.

A typical application is depicted in Figure 2 where the dielectric slit die **1** has been attached to the end of a plastics extrusion machine **14** using four bolts that extend through holes **12** in the steel housing to an adapter plate **13** at the end of the extruder **14**. In this case the properties of the extruded plastic are measured in real-time at the temperature of processing. In addition to the dielectric sensor, two other sensors **31** and **32** are shown in

the setup of Figure 2, and additional sensor ports can be machined into the stainless steel housing. Real-time materials property data can be used for quality control and as measurement values that are utilized in a feedback loop to control the process. All of the active sensors in the slit die have their corresponding detector that is coupled to a computer for data acquisition. For the dielectric measurement, various methods to detect the real and imaginary parts of the dielectric constant can be used. Such methods include a lock-in amplifier to detect amplitude and phase of the current that results from the application of a voltage across the electrodes, or a network analyzer, or a dielectric bridge, or a dielectric spectrometer.

The electrodes of the dielectric sensor are deposited onto an alumina ceramic substrate **4** in an interdigitating pattern of finger electrodes **3**. Two sets of finger electrodes are interwoven to create the sensor as shown in Figure 3. Each set of fingers is connected to a lead electrode **15**, and when an alternating voltage is applied to the electrodes, an electric field fringes between neighboring finger electrodes and extends not only through the alumina ceramic **4** but also into the liquid media flowing above the surface. In practice, the lock-in amplifier is used to measure the dielectric properties of the electroded alumina piece as a function of temperature and frequency when the slit die is empty. These data are stored in a calibration file in the computer. With liquid flowing through the slit **2** and a voltage applied to the electrodes **3**, the value and phase of the resultant current is measured. By subtracting out the current through the alumina, the relative permittivity ε' and dielectric loss ε'' of the liquid media can be determined. The data are recorded as complex dielectric permittivity ε^* where $\varepsilon^* = \varepsilon' - i\varepsilon''$. The measurement procedure was developed by McBrearty and Perusich.

Because the fringing field is strongest near the surface, the sensitivity of the dielectric sensor is biased toward the surface. The spatial extension of the electric field into the media under investigation is determined by the spacing between the electrode fingers. The field decreases in strength exponentially with distance from the surface with a characteristic length $\lambda/3$ where λ is the distance between neighboring electrodes. To measure dielectric properties near the surface, a small value of λ is needed. Conversely,

to allow the field to reach into the bulk of the flowing media, a relatively large value of λ is needed. Thus, if λ is 1 mm, then the field strength decays with a characteristic dimension 0.33 mm and the farthest extension of the field is approximately 1.5 mm. To extend the field farther into the flowing liquid by making λ larger has its limits because, as λ increases, the capacitance of the cell decreases compromising the sensitivity of the sensor. An appropriate balance between sensitivity and the spatial extent of the field must be taken in account when designing the electrode pattern. The slit height is set to be larger than the outward reach of the fringing field, so that the dielectric properties of the ceramic piece **10** in the upper half of the slit die are not a factor in the measurement. In order to sample a significant fraction of the cross section of the flowing liquid, the current embodiment of the slit die is designed with a 2 mm slit height and $\lambda = 0.5$ mm, but these dimensions can be changed by cutting the slit height in the upper ceramic piece to a different size and using a different electrode pattern.

The design of the dielectric slit die permits interchangeable ceramic substrates with different electrode patterns and electrode separation λ. The electrodes are deposited and fired on a flat surface making it convenient for depositing different electrode patterns. For example, the dual electrode patterns **16** shown in Figure 4a can be used to measure simultaneously near surface dielectric properties as well as bulk properties because the two patterns have significantly different electrode separation. Figure 4b displays patterns **17** oriented at 90° to each other for the purpose of investigating orientation effects in a liquid of high viscosity undergoing shear flow. The alumina ceramic **4** is positioned in a well that has been machined into the bottom half stainless piece **6** and is held mechanically in place by clamping top and bottom halves together. No epoxy or other adhesive is needed. To change ceramic substrates, the alumina block is removed from its well using the lifting bolts **18** on the bottom of the housing to push the block out of the well. It can be replaced with electroded alumina substrates with different electrode patterns. Likewise, the ceramic piece **10** with the cut-out slit in the top half of the sensor can be interchanged with pieces having different slit sizes.

The slit configuration accomplishes three objectives: first, it confines the flowing liquid to a thin ribbon for which a significant fraction of its cross section is intersected by the fringing electric field lines; second, the slit defines a sample chamber of fixed dimensions along which other sensors can be positioned; and third, it is the geometry of a slit die rheometer so that with knowledge of the pressure drop across the length of the slit and the volume flow rate, the viscosity of the material can be determined. The pressure transducer is positioned upstream from the dielectric sensor and yields the value of the pressure drop along the axial length of the slit **2**.

The optics sensor, shown in Figure 5, is situated upstream from the dielectric sensor in the stainless steel portion of the slit die. It consists of a bundle of seven 200 μm core optical fibers **33** that are placed into a sleeved half-inch sensor bolt **19** with a sapphire window **20** at its end. It operates in the reflection mode, i.e. one of the fibers **34,** shown in Figure 6**,** transmits light from the light source **21** (that has been confined to a narrow wavelength band by a filter **22**) through a focusing lens **23**, the sapphire window **20**, the flowing liquid, reflects off the far stainless steel surface, and reverses its path through the material, sapphire window **20** and lens **23**. The reflected light is collected by the other six fibers **35** and is transmitted to the photomultiplier (PMT) detector **24** as shown in Figure 6. The intensity of the light source **21** is monitored using a beamsplitter **25** that sends a source sampling beam to another photomultiplier (PMT) **26**. The ratio of the two light intensities is used to monitor the light transmission through the liquid. In this manner fluctuations in light source intensity are cancelled out. The light sensor can also be used for fluorescence monitoring where the single optical fiber transmits the excitation light to the flowing liquid, and fluorescence collected by the six fibers is transmitted to a monochromator **27**. For fluorescence detection, the monochromator substitutes for the PMT **24** in Figure 6.

A machined flat at the back end of the slit die is reserved for an ultrasonics sensor **28**. In this position, the ultrasonic sensor functions in a manner similar to the optical sensor, i.e. in the reflection mode. A transducer placed on the flat area transmits an ultrasonic wave through the stainless steel housing, through the material under investigation, reflecting

off the far stainless steel wall, reversing its direction, taking a second pass through the material and returning through the stainless steel to the transducer that acts as both transmitter and detector. Using standard ultrasonics detection equipment, both the attenuation of the ultrasonic energy and the velocity of the wave in the examined material can be measured. Ultrasonics velocity is related to the bulk modulus of the material and the attenuation of ultrasonics energy is related to absorption and scattering of the ultrasonics wave.

As shown in Figure 7, additional instrumentation port sectors **29** can be added in-line with the slit die **1**, sandwiched between the extruder **14** with the adapter plate **13** and the slit die. These sectors can have standard half-inch instrumentation ports or have a custom port configuration for special sensors **36** such as opposing optical windows that are used for IR and UV spectroscopy. The instrument port sectors can be placed in service as the need for new data arises.

EXAMPLE 1

To demonstrate the operation of the dielectric slit die, we show the results, in Figure 8, of single screw compounding of nylon 12 with 4 % smectite clay. Figures 8a and 8b show real-time data for extrusion of nylon 12 (neat) and for nylon 12 compounded with 4 % clay. Compounding was carried out at 195 °C. Relative permittivity and conductivity are plotted versus time for fifteen different frequencies ranging from 500 Hz to 100 kHz. At t = 400 s, the neat polymer entered the electrode region of the dielectric sensor and was extruded for approximately 1500 s, at which time resin pellets mixed with 4 % mass fraction of clay were added to the feeder. Permittivity and conductivity began to increase as the mixture filled the slit region, and after significant transition time, the data reached a plateau value. The transition is associated with time it takes the clay/polymer mixture to completely fill the sensing region, particularly at the surface near the electrodes. At t = 4200 s, the neat resin was again introduced and relative permittivity values returned to their original values.

The difference in relative permittivity at low frequency (500 Hz) and high frequency (10^5 Hz) is called the dielectric dispersion. We see that the dispersion for the clay/polymer nanocomposite is considerably larger than that for the neat polymer. This is because clay particles introduce ionic species into the resin mixture that contribute to conductivity and polarization over and above that which is present in the neat resin.

Figures 9a and 9b show pressure and optical signals as a function of time corresponding to the time scale of Figures 8a and 8b. Steady state conditions prevail after the transitions are complete. The optical transmission data are expressed as I/I_o where I is the intensity of light transmitted through the extruded resin in the slit and I_o is the intensity of the light source. The optical data show attenuation of the optical beam as it transmits through the neat and clay filled nylon. These data can be correlated with the volume fraction and microstructure of clay in nylon 12. Steady state pressure in conjunction with the volume flow rate can be use to calculate an apparent viscosity using equations for liquid flow through a slit die. In this case apparent viscosity values of 139 Pa.s and 164 Pa.s were obtained for the neat and clay filled nylon 12 at 195 °C respectively.

EXAMPLE 2

Real-time fluorescence monitoring is illustrated in Figure 10. Here, polyethylene vinyl acetate copolymer, containing a low concentration of the fluorescent dye benzoxazolyl stilbene, was extruded through the slit and the fluorescence spectrum was detected using a monochromator as illustrated in Figure 6. The spectra can be used to determine machine residence time and resin temperature.